Joint Development and Coordination of Emissions Control Data and Models (CLEERS Analysis and Coordination)

Stuart Daw, Josh Pihl, Jae-Soon Choi,
Bill Partridge, Todd Toops, Vitaly Prikhodko,
Charles Finney, Will Brookshear

project ID:
ACE022

PI: **Stuart Daw**
Presenter: **Josh Pihl**
Oak Ridge National Laboratory

DOE Vehicle Technologies Office
Annual Merit Review & Peer Evaluation Meeting
June 8, 2016
Washington, DC

DOE Managers:
Ken Howden, Gurpreet Singh, Leo Breton

ORNL is managed by UT-Battelle
for the US Department of Energy

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Overview

Timeline

Project start date: FY2016

Project end date: FY2018

- included in ORNL response to 2015 VTO “Lab Call”
- core activity since FY2000
- supports and coordinates emissions control research
- evolves with DOE priorities and industry needs

Budget

	FY15	FY16
Coordination	$236k	$250k
Analysis	$377k	$400k

Barriers

MYPP Challenges and Barriers:

- 2.3.1.B Lack of cost-effective emission control
- 2.3.1.C Lack of modeling capability for ... emission control
- 2.3.1.E Durability (of emissions control devices)

MYPP Technical Targets:

- EPA Tier 3 Emissions (original goal: Tier 2 Bin 2)
- <1% efficiency penalty due to emission control

Partners

- DOE Advanced Engine Crosscut Team
- U.S.DRIVE ACEC Team
- CLEERS Focus Group members
  - 10 engine/vehicle manufacturers
  - 12 component and software suppliers
  - 11 universities
- PNNL, Politecnico di Milano, UCT Prague

CLEERS enables the DOE VTO goals of improving efficiency while meeting emissions regulations

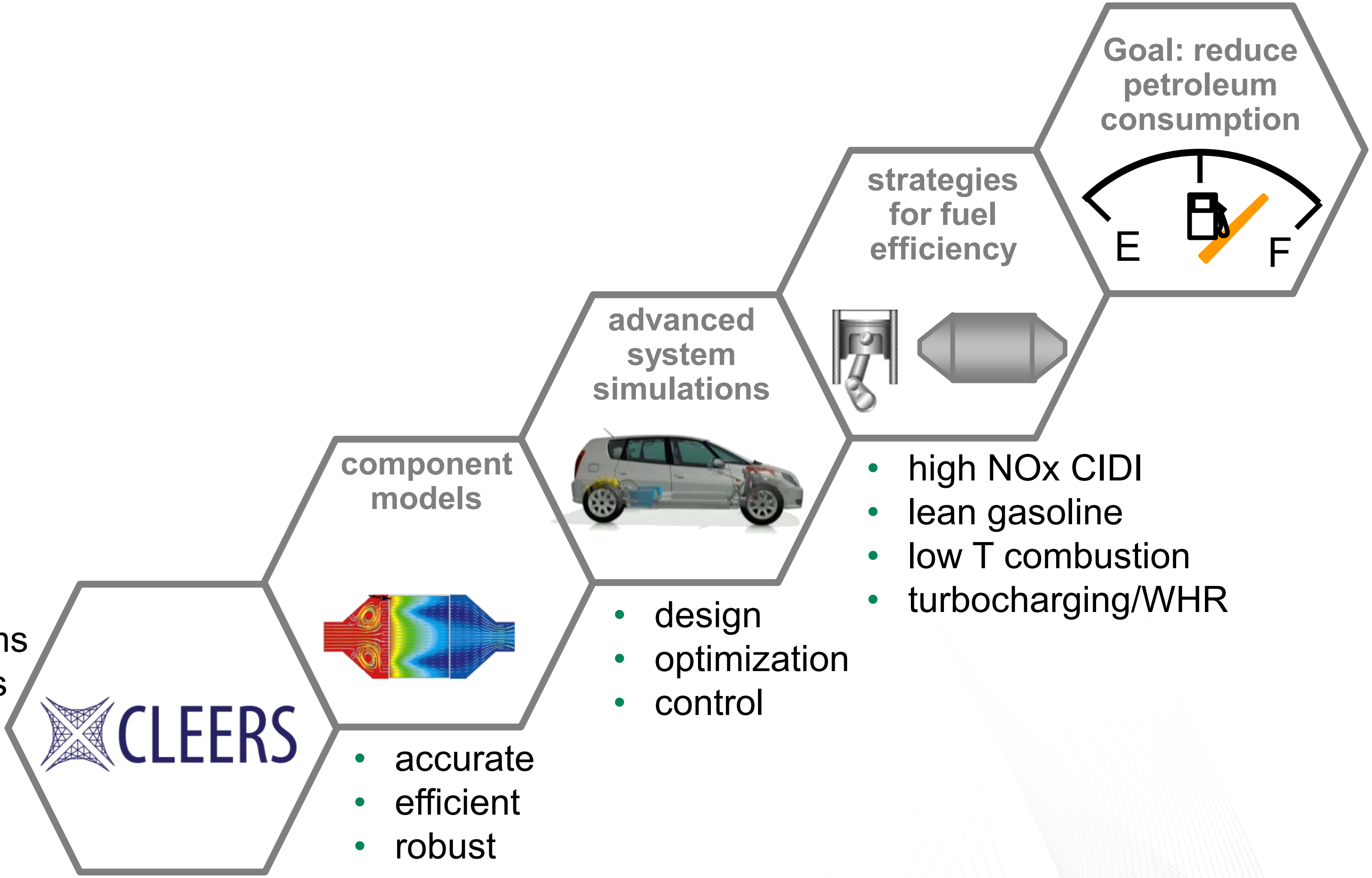
"The [VTO ACE] R&D approach is to *simultaneously improve engine efficiency and meet future federal and state emissions regulations through* a combination of combustion and fuels technologies that increase efficiency and minimize in-cylinder formation of emissions, and *cost effective aftertreatment technologies* to further reduce exhaust emissions *with minimal energy penalty*."

- Vehicle Technologies Office Multi-Year Program Plan

- CLEERS = **C**rosscut **L**ean (/**L**ow-temperature) **E**xhaust **E**missions **R**eduction **S**imulations
- CLEERS mission: accelerate the development of emissions control technologies for advanced engines by improving the accuracy of aftertreatment system simulations
- CLEERS objectives:
  - support collaborations among industry, university, national lab partners
  - develop and disseminate pre-competitive data, parameters, and models
  - gather feedback from industry on critical emissions control research needs
  - coordinate DOE National Laboratory research efforts

CLEERS provides a key stepping stone on the path to reduced petroleum consumption

- strategies
- mechanisms
- parameters
- protocols
- data

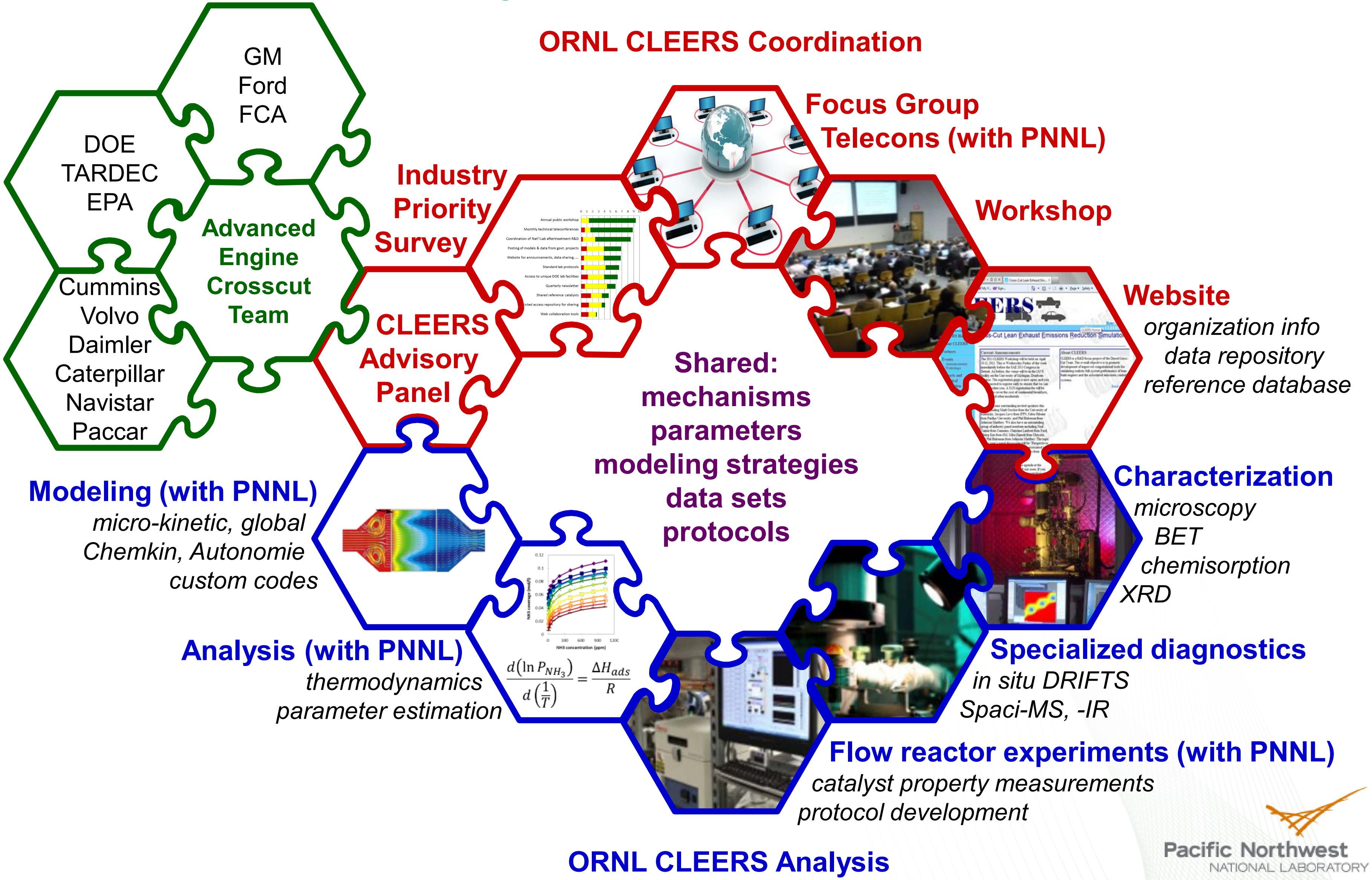


- accurate
- efficient
- robust

- design
- optimization
- control

- high NOx CIDI
- lean gasoline
- low T combustion
- turbocharging/WHR

ORNL coordinates CLEERS activities and conducts R&D in support of CLEERS objectives



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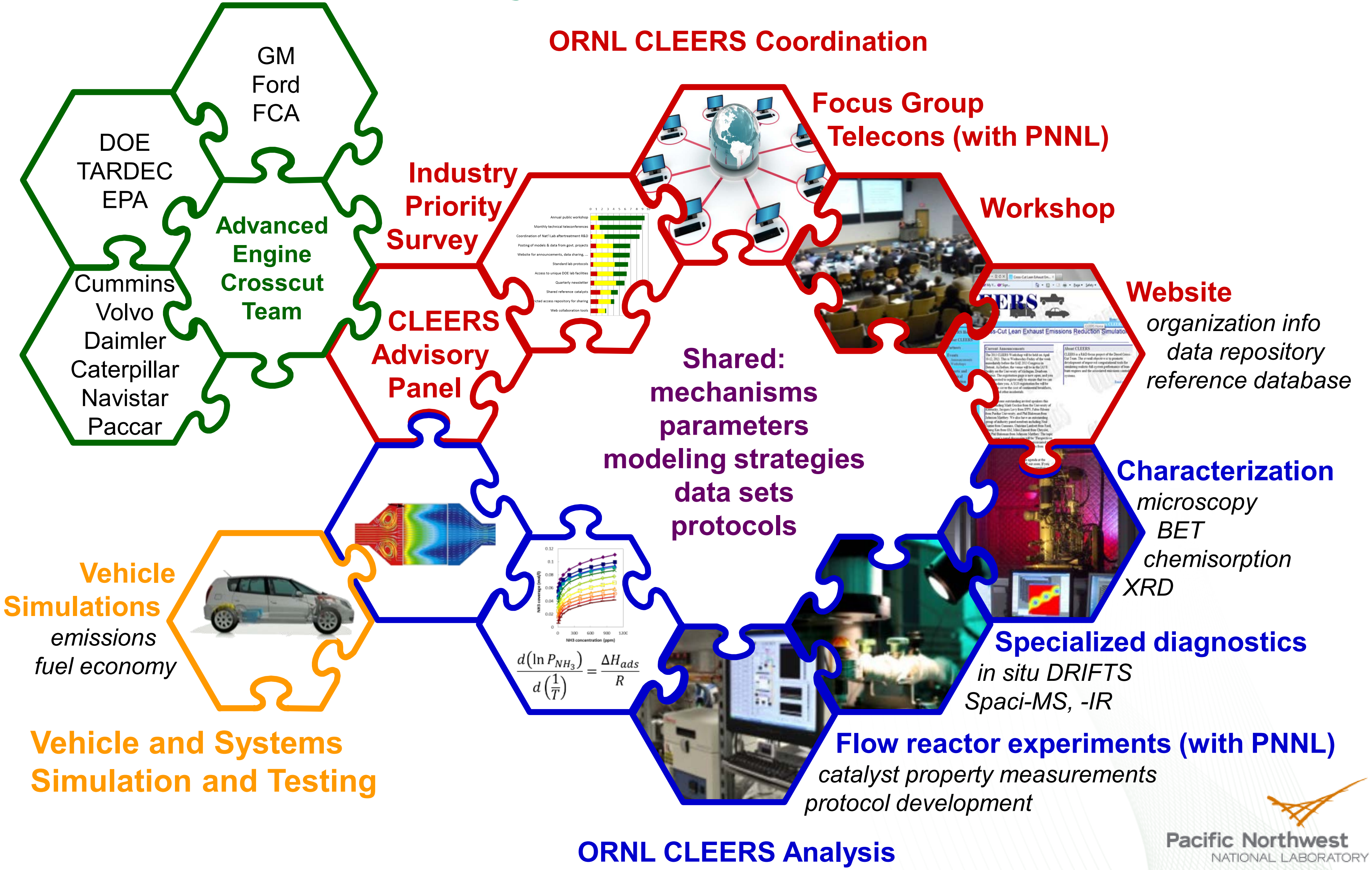
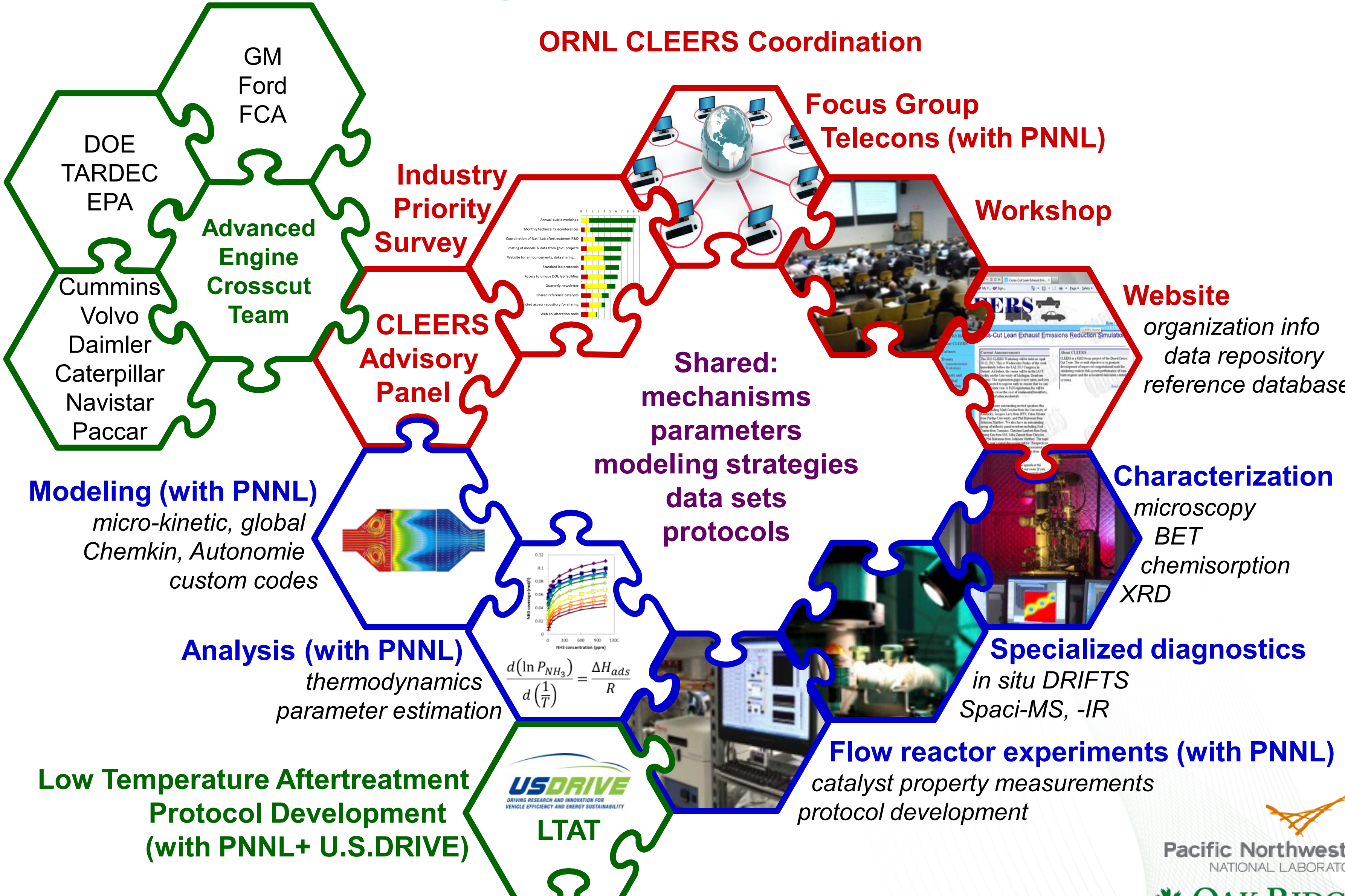


Pacific Northwest NATIONAL LABORATORY

OAK RIDGE National Laboratory

ORNL coordinates CLEERS activities and conducts R&D in support of CLEERS objectives



Pacific Northwest NATIONAL LABORATORY

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Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap Powertrain Technologies

Low Temperature Combustion

Dilute Gasoline Combustion

Clean Diesel Combustion

CLEERS (ACE022)
Coordination
Experiments, Analysis, Modeling

Low Temperature Catalysis (ACE085)

Lean Gasoline Emissions Control (ACE033)

Emissions Control CRADA with Cummins (ACE032)

Program Management Support

Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap Powertrain Technologies

Low Temperature Combustion

Dilute Gasoline Combustion

Clean Diesel Combustion

CLEERS (ACE022)
Coordination
Experiments, Analysis, Modeling

Provide Guidance from CLEERS Industry Priority Survey

Present at CLEERS Workshop, telecons; Post data sets on CLEERS website

Low Temperature Catalysis (ACE085)

Lean Gasoline Emissions Control (ACE033)

Emissions Control CRADA with Cummins (ACE032)

Enabling Fuel Efficient Engines by Controlling Emissions (ORNL FEERC response to 2015 VTO AOP Lab Call)

ACEC Roadmap Powertrain Technologies

Low Temperature Combustion

Dilute Gasoline Combustion

Clean Diesel Combustion

CLEERS (ACE022)
Coordination
Experiments, Analysis, Modeling

Adsorption / desorption / reaction on low T traps

Low Temperature Catalysis (ACE085)

NH_3 formation on PGM catalysts
NH_3 storage/release on SCR catalysts

Lean Gasoline Emissions Control (ACE033)

NH_3 storage/release on SCR catalysts
Aging effects on SCR catalysts

Emissions Control CRADA with Cummins (ACE032)

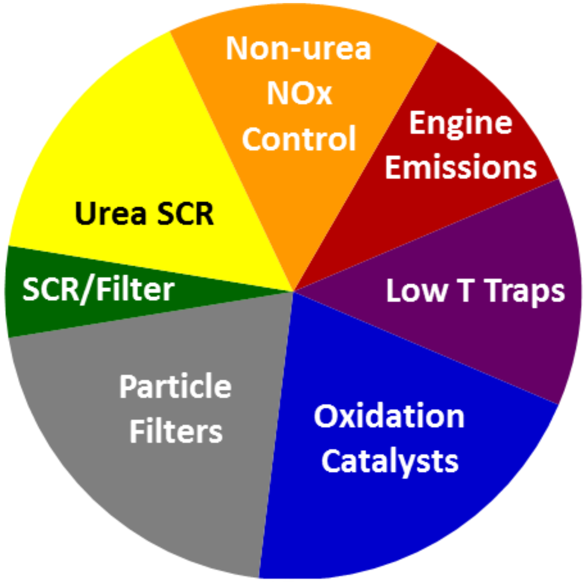
Milestones

FY	Qtr	Milestone	Status
2015	2	Measure impact of catalyst aging on NH_3 storage isotherms and model parameters	complete
2015	3	Conduct 2015 CLEERS Workshop	complete
2016	3	Host 2016 CLEERS Workshop	complete
2016	4	Complete characterization of NH_3 storage on two primary commercial SCR catalysts (Cu-SSZ-13 & Cu-SAPO-34), publish findings, and post NH_3 isotherm data on the CLEERS website	on schedule

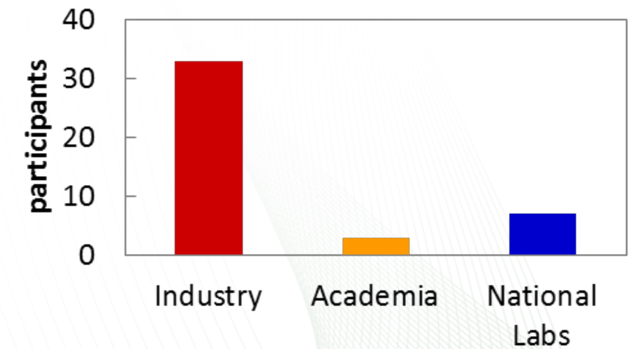
CLEERS is an efficient means for communicating pre-competitive information

- **Workshop #19, April 6-8, 2016, Ann Arbor, MI** ✓ *(milestone)*
  - 140 attendees: OEMs, component & software suppliers, national labs, universities, government representatives
  - 39 presentations, 24 posters
    - Record number of abstract submissions
  - Panel discussion on “Meeting Tier 3 and the potential future impact of on-board emissions measurements and real-world/on-road emissions standards”
- **Focus Group teleconferences:**
  - Technical presentations of latest results
  - 20-60 invited participants from around globe
    - typically >50% industry representatives
- **Industry communication and scoping:**
  - 2015 Industry Priorities Survey
    - results posted on CLEERS website with prior reports
  - Assistance to U.S.DRIVE ACEC Tech Team Low Temperature Aftertreatment working group
    - protocols available on CLEERS website

2016 CLEERS Workshop Presentation Topics

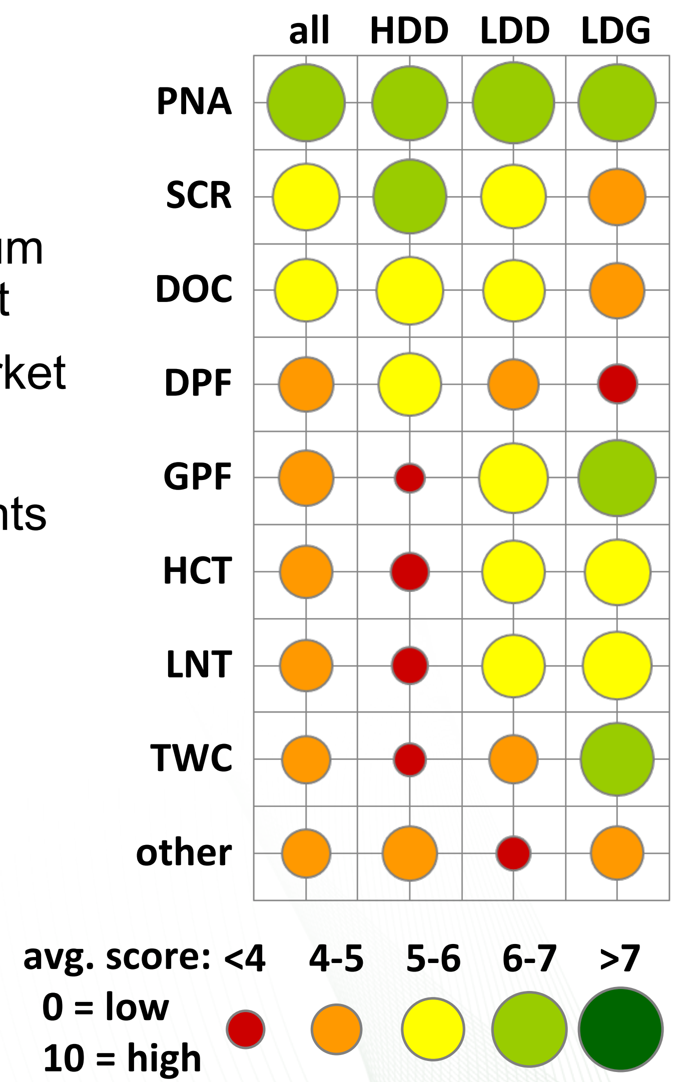


January 2016 Focus Group Teleconference Participants



2015 Priority Survey revealed interest in a wide range of technologies, with particular emphasis on low T approaches

- Responses reveal a diversity of opinions among survey participants:
  - every technology listed in poll was ranked medium priority or higher for at least one market segment
  - priorities vary by market segment, and each market segment has multiple high priority technologies
- PNAs generated interest across all market segments
- Two cross-cutting high priority themes emerged repeatedly:
  - new low temperature catalyst formulations
  - formation of greenhouse gas byproducts



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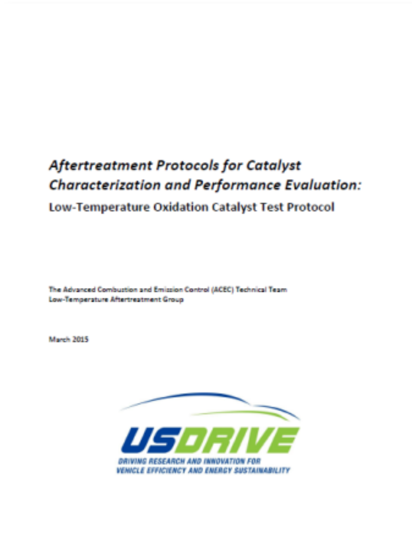
Supported the U.S.DRIVE ACEC LTAT team in developing and testing experimental protocols for low T catalysts

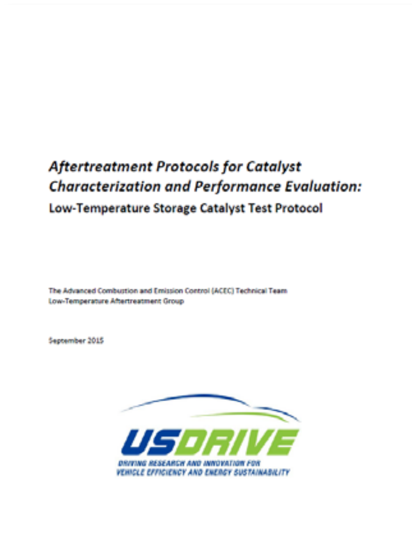


Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:
Low-Temperature Oxidation Catalyst Test Protocol

The Advanced Combustion and Emission Control (ACEC) Technical Team
Low-Temperature Aftertreatment Group

March 2015

USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY



Aftertreatment Protocols for Catalyst Characterization and Performance Evaluation:
Low-Temperature Storage Catalyst Test Protocol

The Advanced Combustion and Emission Control (ACEC) Technical Team
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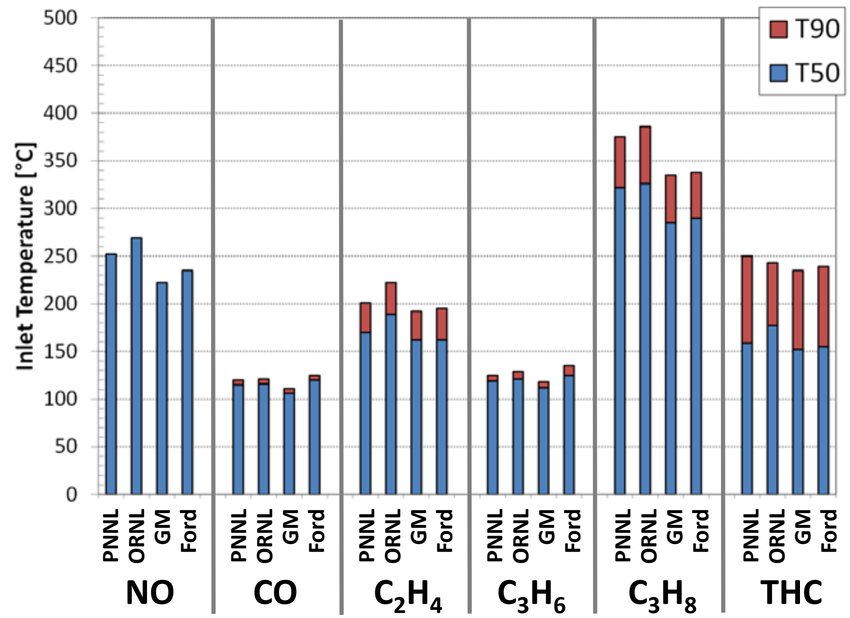
September 2015

USDRIVE
DRIVING RESEARCH AND INNOVATION FOR VEHICLE EFFICIENCY AND ENERGY SUSTAINABILITY



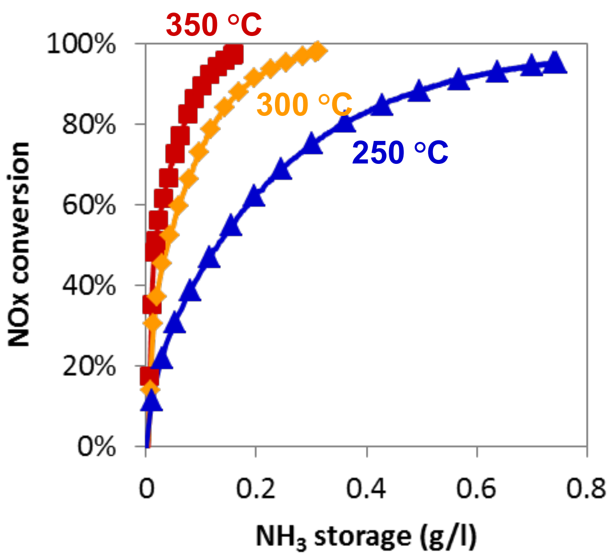
Org.	Representatives
FCA	Craig DiMaggio
Ford	Joe Theis
GM	Se Oh Wei Li
PNNL	Ken Rappe Mark Stewart
ORNL	Jim Parks Josh Pihl
UM	Galen Fisher
DOE	Ken Howden

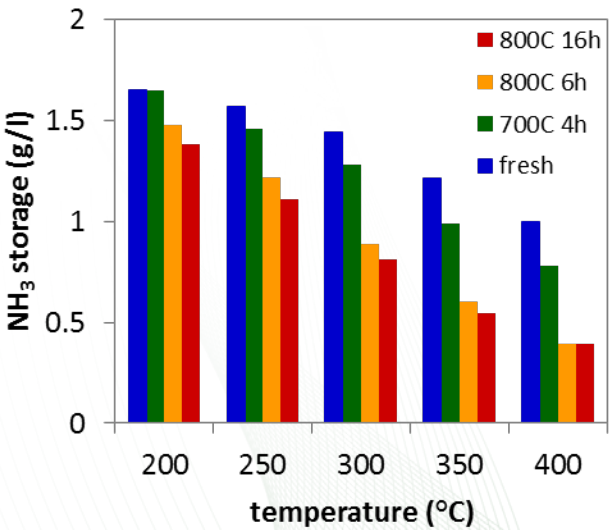
- Participated in round robin testing of OC protocol
  - evaluated impact of reactor setup
    - example: inert core upstream of catalyst has no effect
  - identified protocol revisions to improve clarity
  - shared data with members of LTAT team for comparison of reproducibility across labs
- Supported development of a trap protocol

Accurate models of NH_3 storage needed to develop high NOx conversion SCR systems

collaboration with PNNL

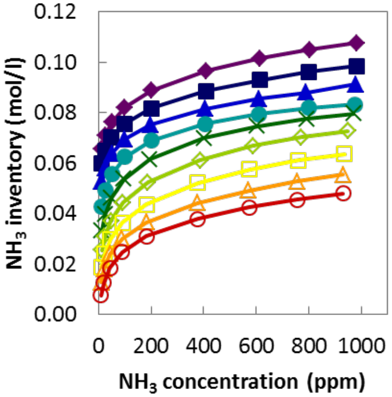
- Priority Survey: within heavy duty diesel market segment
  - NH_3 storage/oxidation/release: #10 of all 64 topics
  - SCR aging mechanisms & models: #4 of all 64 topics
- NH_3 inventory must be managed to maximize NOx conversion, minimize NH_3 slip, efficiently utilize urea
  - high NH_3 coverages required for high NOx conversion
  - critical for approaches based on NH_3 production/consumption cycles (passive SCR, LNT-SCR)
  - dosing strategies often built with simulation tools
- NH_3 storage capacity varies significantly with temperature, gas composition, and catalyst age
  - models must capture these dependencies
- Challenges in current measurement & modeling strategies:
  - model uncertainty: site multiplicity, adsorption energetics
  - confounded TPD data: thermodynamics, kinetics, transport
  - resulting parameters neither global nor universal





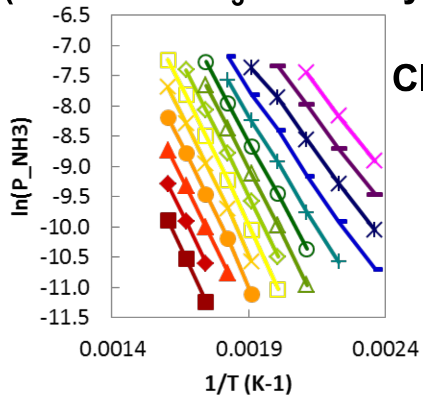
Steady state isotherms and thermodynamic analysis isolate SCR NH_3 adsorption energetics, guide model development

NH_3 adorption isotherms



remap data

$\ln(P_{NH3})$ vs. 1/T (at const. NH_3 inventory)

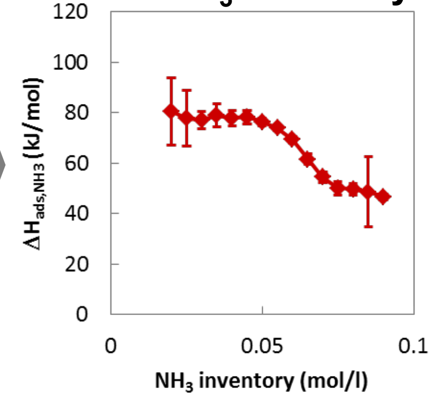


Clausius-Clapeyron Equation:

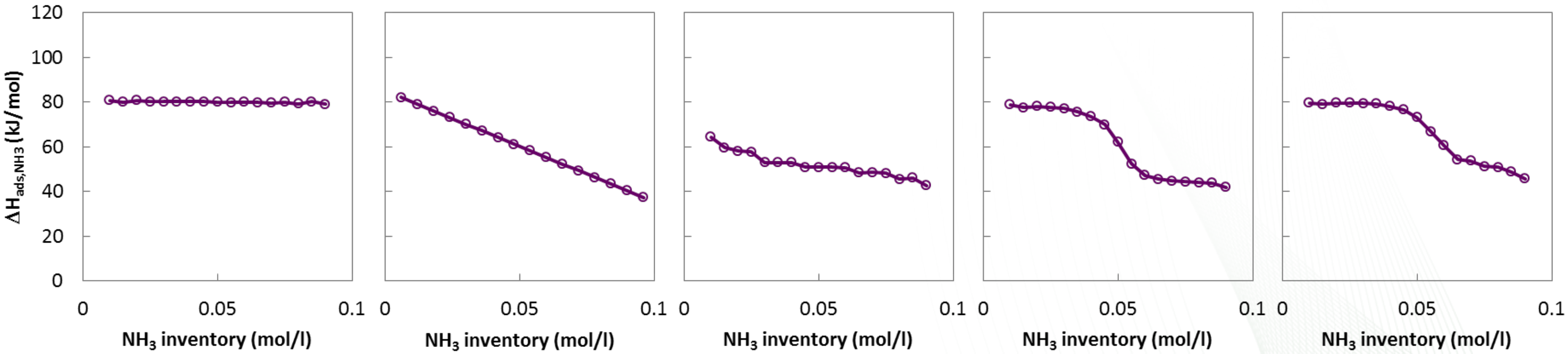
$$\frac{d\,ln(P)}{d\left(\frac{1}{T}\right)} = \frac{-\Delta H_{ads}}{R}$$

slope = enthalpy

adsorption enthalpies vs. NH_3 inventory



# sites:	**1**	**1**	**1**	**2**	**2**
isotherm:	**Langmuir**	**Temkin**	**Langmuir**	**Langmuir**	**Langmuir**
# H_2O sites:	**0**	**0**	**1**	**0**	**1**



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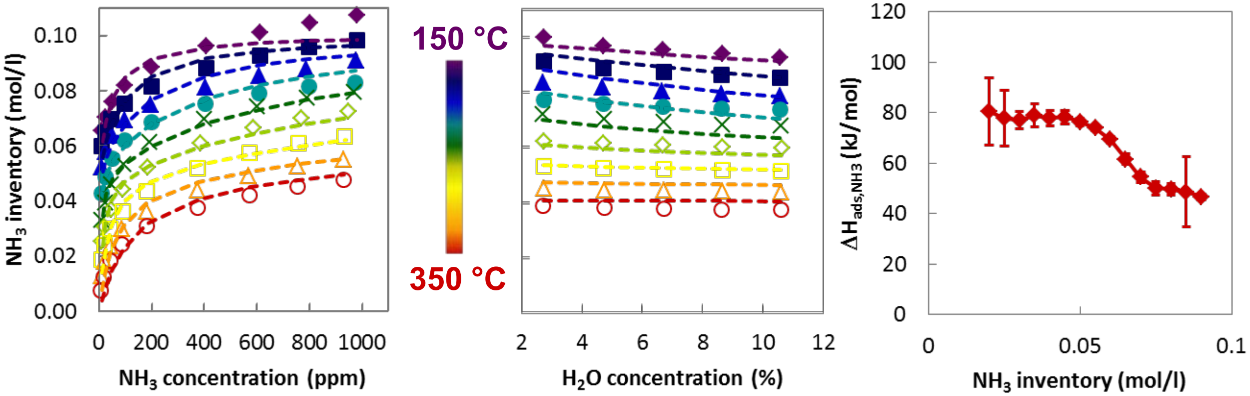
Same model structure can be applied to two different commercial urea SCR formulations (Cu-SAPO-34, Cu-SSZ-13)

Cu-SSZ-13 (GM Pickup Truck)



site	1	2
ω (mol/l)	0.050	0.050
$K_{i,NH3,0}$	1.8E-3	3.0E-5
$\Delta H_{i,NH3}$ (kJ/mol)	-80	-79
$K_{i,H2O,0}$	--	9.4E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-42

- Two NH_3 storage sites

$$I_{NH_3} = \omega_1\theta_{1,NH_3} + \omega_2\theta_{2,NH_3}$$

- Langmuir isotherm for both sites

$$\theta_1 = \frac{K_{1,NH_3}P_{NH_3}}{1 + K_{1,NH_3}P_{NH_3}}$$

  – H_2O competition (site 2 only)

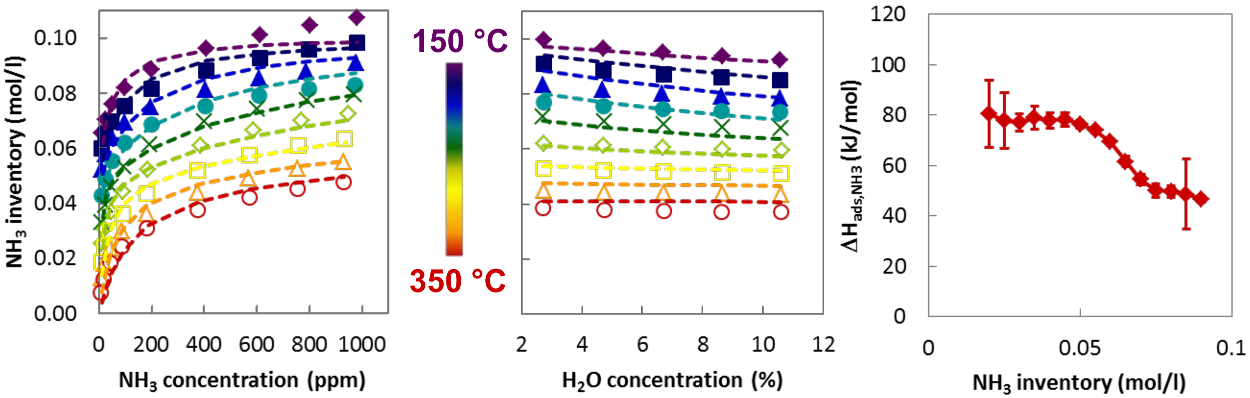
$$\theta_2 = \frac{K_{2,NH_3}P_{NH_3}}{1 + K_{2,NH_3}P_{NH_3} + K_{2,H_2O}P_{H_2O}}$$

- Constant ΔH_{ads} for each site

$$K_{i,s} = K_{i,s,0}e^{-\Delta H_{i,s}/RT}$$

Same model structure can be applied to two different commercial urea SCR formulations (Cu-SAPO-34, Cu-SSZ-13)

Cu-SSZ-13 (GM Pickup Truck)

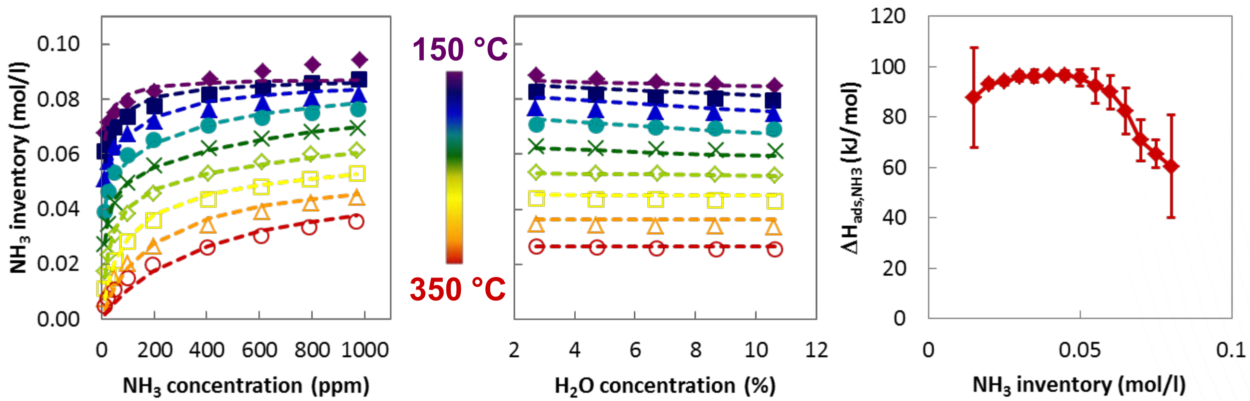


site	1	2
ω (mol/l)	0.050	0.050
$K_{i,NH3,0}$	1.8E-3	3.0E-5
$\Delta H_{i,NH3}$ (kJ/mol)	-80	-79
$K_{i,H2O,0}$	--	9.4E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-42

- Isotherm shapes, H_2O dependence look very similar
- ΔH_{ads} vs. inventory indicates two distinct sites

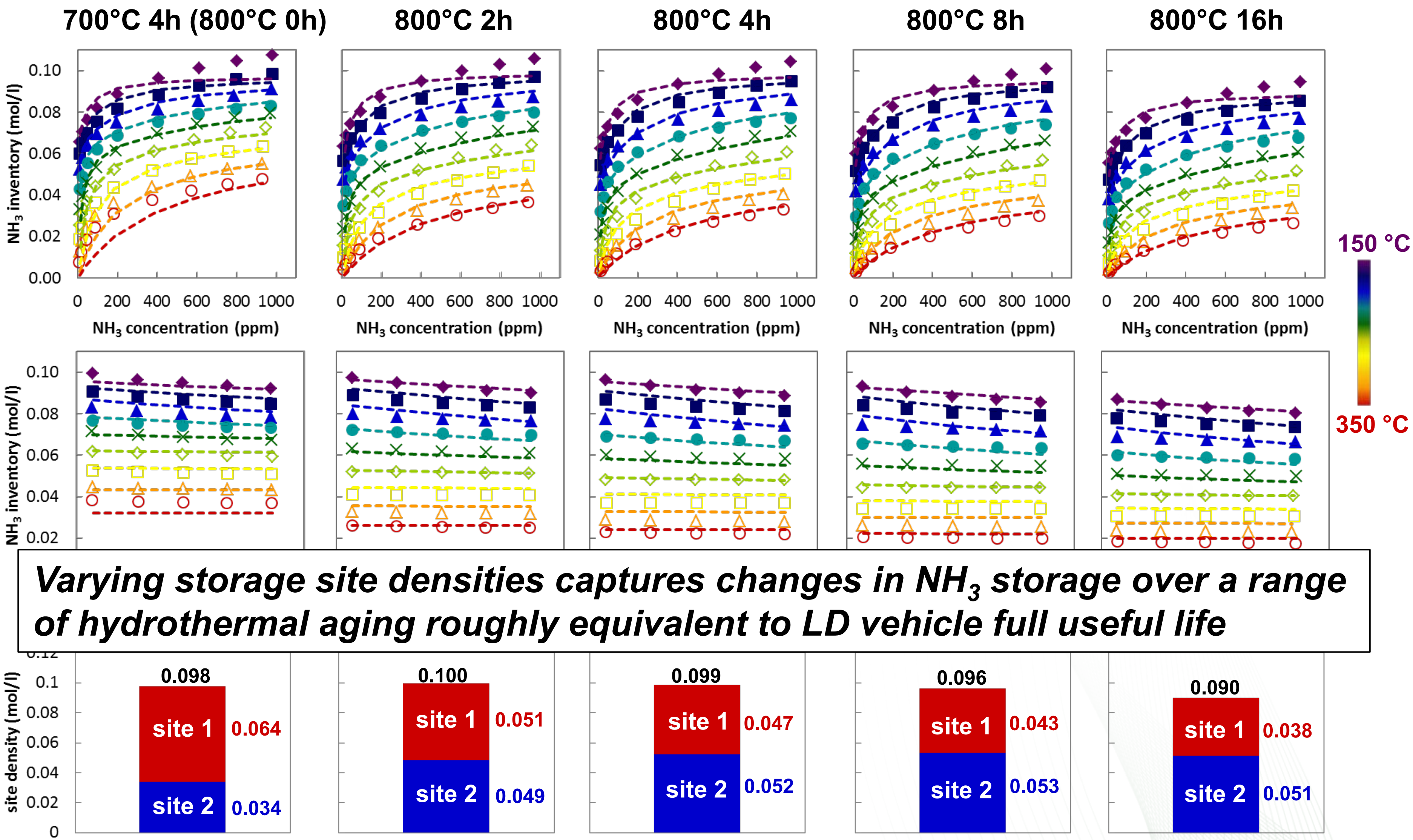
model structure works well for two different Cu zeolite SCR formulations

Cu-SAPO-34 (Cummins ISB engine) ✓*(milestone)*



site	1	2
ω (mol/l)	0.050	0.037
$K_{i,NH3,0}$	2.7E-5	9.9E-8
$\Delta H_{i,NH3}$ (kJ/mol)	-95	-102
$K_{i,H2O,0}$	--	1.4E2
$\Delta H_{i,H2O}$ (kJ/mol)	--	-55

Impact of Cu-SSZ-13 hydrothermal aging captured by changing site densities while holding other parameters fixed



Varying storage site densities captures changes in NH_3 storage over a range of hydrothermal aging roughly equivalent to LD vehicle full useful life

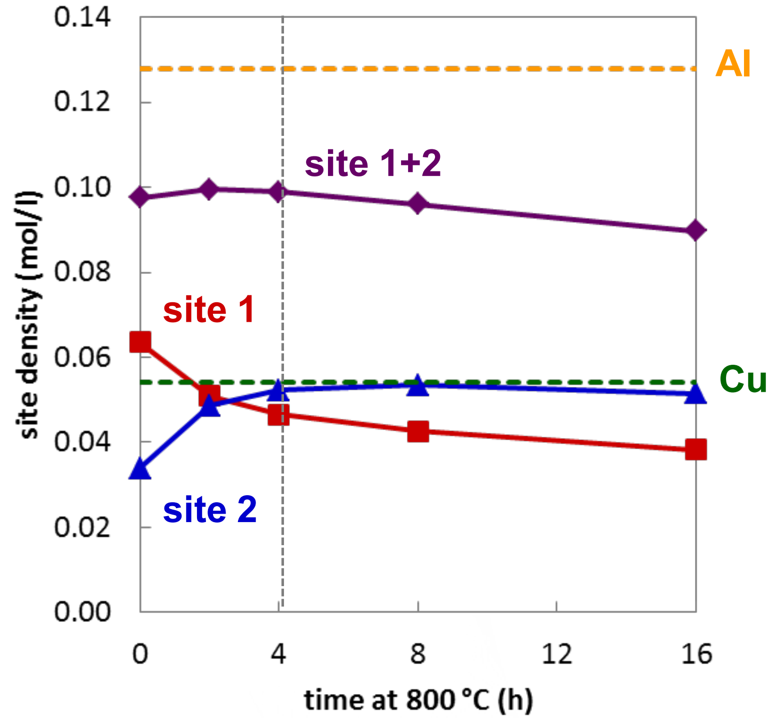
Changing site densities provide a method for modeling aging effects and perhaps understanding aging mechanisms

- Parameter estimation process after aging:
  - fix adsorption energetics across all steps
  - allow site densities to vary with aging
- Hydrothermal aging at 800 °C appears to occur over two distinct phases:

	aging time	NH_3 storage site 1	2	total	
Phase I	<4 h	⇩	⇧	⇔	site 1 ➡ site 2
Phase II	>4 h	⇩	⇔	⇩	loss of site 1

- Proposed physical sites:
  - site 1: zeolite Brønsted acid sites
  - site 2: Lewis acid sites (likely Cu)

Correlating model sites with catalyst physical sites yields insights into aging mechanisms and simulation strategies



site	1	2
ω (mol/l)	f(age)	f(age)
$K_{i,NH3,0}$	3.1E-3	5.2E-6
$\Delta H_{i,NH3}$ (kJ/mol)	-84	-85
$K_{i,H2O,0}$	--	2.9E-4
$\Delta H_{i,H2O}$ (kJ/mol)	--	-44

Collaborations

CLEERS Technology Focus Group

Advanced Engine Crosscut Team

ACEC Tech Team

DOE VTO

HD OEMs:
Caterpillar
Cummins
Daimler Trucks
Navistar
Paccar
Volvo

LD OEMs:
FCA
Ford
GM

EPA
TARDEC

Suppliers:
BASF
Johnson-Matthey
Umicore
Corning
Delphi
Eaton
Haldor Topsoe

CLEERS Industry Survey Recipients

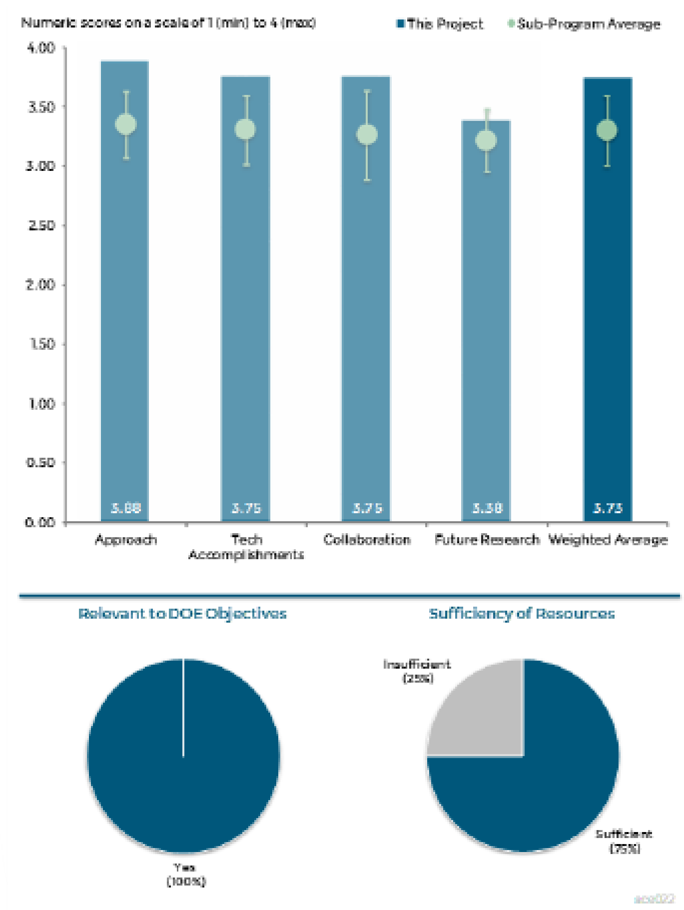
Universities:
Chalmers Univ.
Michigan Technological Univ.
Pennsylvania State Univ.
Politecnico di Milano
Purdue University
Texas A&M Univ.
UCT Prague
Univ. of Houston
Univ. of Kentucky
Univ. of Notre Dame
Univ. of Michigan
Univ. of Wisconsin

National Labs:
ORNL
PNNL
ANL
LANL

Industry:
John Deere
Bosch
Tenneco
IAV
Gamma
N2Kinetics
Emissol

Responses to Reviewer Comments

Reviewer Comments:	Responses:
• Extend CLEERS Workshop time slots to 25 min to allow more time for discussion	• 2016 Workshop agenda extended to 3 full days to allow for 25 minute time slots
• Investigate other emissions control topics in addition to NH_3 storage capacity of SCR catalysts and N_2O from LNTs • Start passive NOx adsorber investigations concurrently with hydrocarbon trap research	• Investigations into both hydrocarbon traps and passive NOx adsorbers will begin in FY2016
• Investigate physical characteristics that lead to low energy/high energy NH_3 storage sites	• Correlations with physical sites already under way • Future model catalyst investigations will generate more insights



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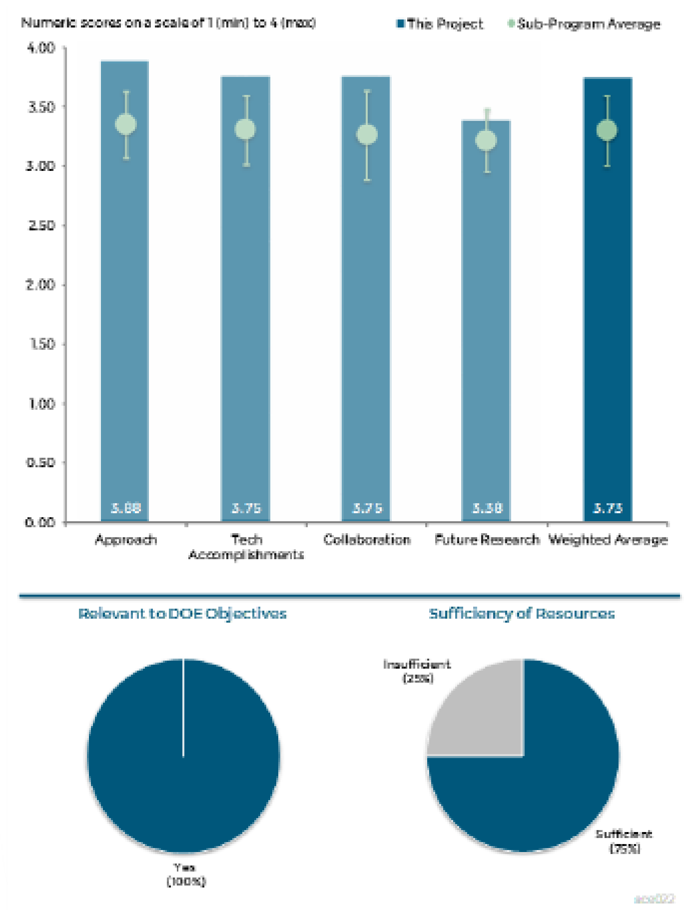

relevance approach accomplishments collaborations future work

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Remaining Challenges & Barriers/Future Work

Remaining Challenges:	Future Work:
• Decreasing exhaust temperatures from higher efficiency engines and advanced combustion modes.	• Continue emphasizing low T emissions control priorities in CLEERS activities and plans • Identify modeling strategies and key parameters for passive adsorber devices • Develop CLEERS HC and NOx adsorber protocols and begin experimental characterization
• Requirements for higher NOx conversion efficiencies coupled with limited accuracy of available NH_3 SCR device models, particularly for predictions of NH_3 inventories.	• Refine simple, accurate NH_3 storage modeling and parameter estimation strategies based on adsorption isotherms • Expand NH_3 storage measurements and modeling to other catalyst formulations
• Ongoing need for coordination and collaboration in developing simulation tools for next generation emissions control devices.	• Continue planning, teleconference, workshop, website, and DOE lab coordination activities

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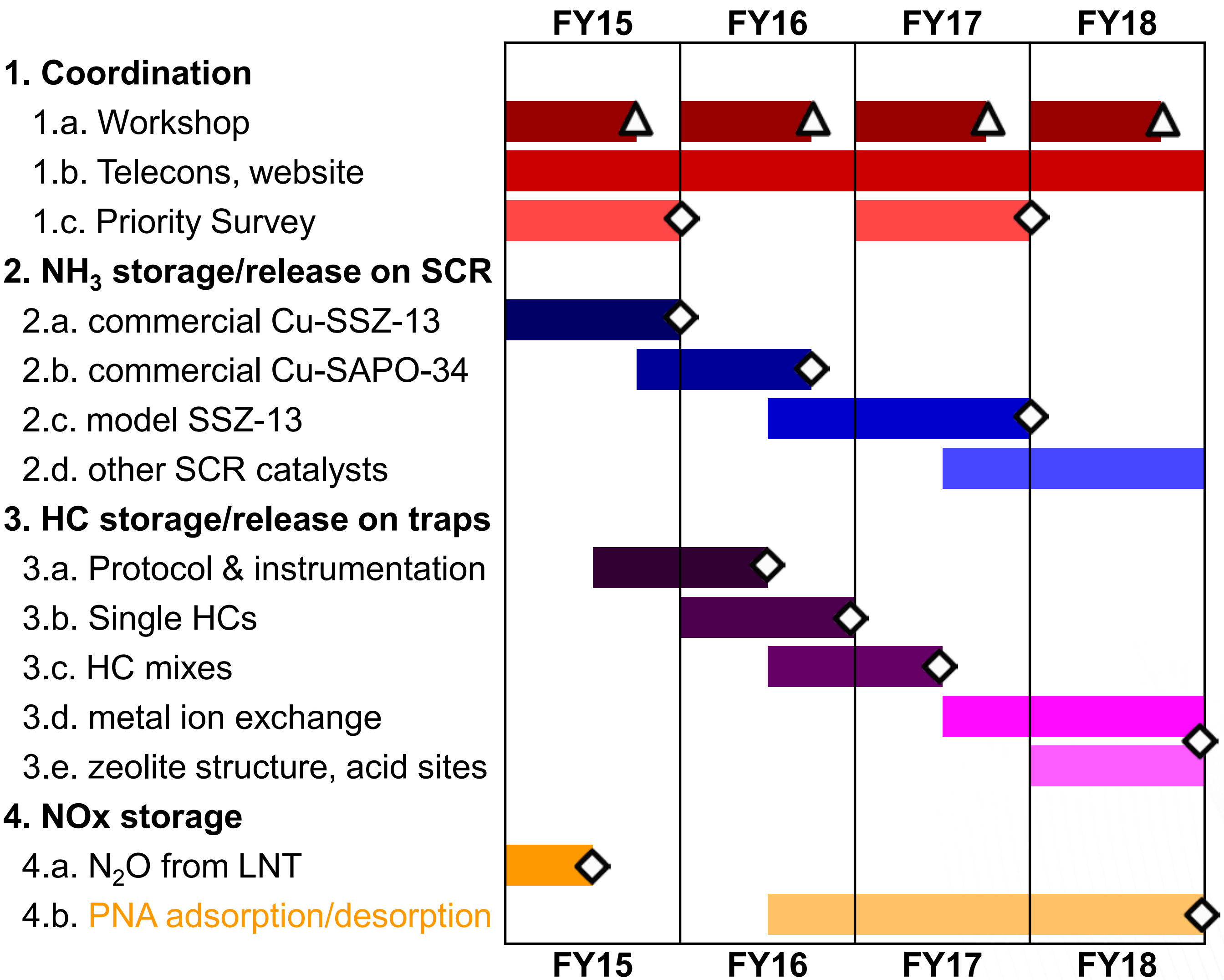
Proposed schedule for ORNL CLEERS activities includes an increasing emphasis on adsorbers for low T applications



Note: schedule contingent on funding availability, DOE program needs, industry feedback

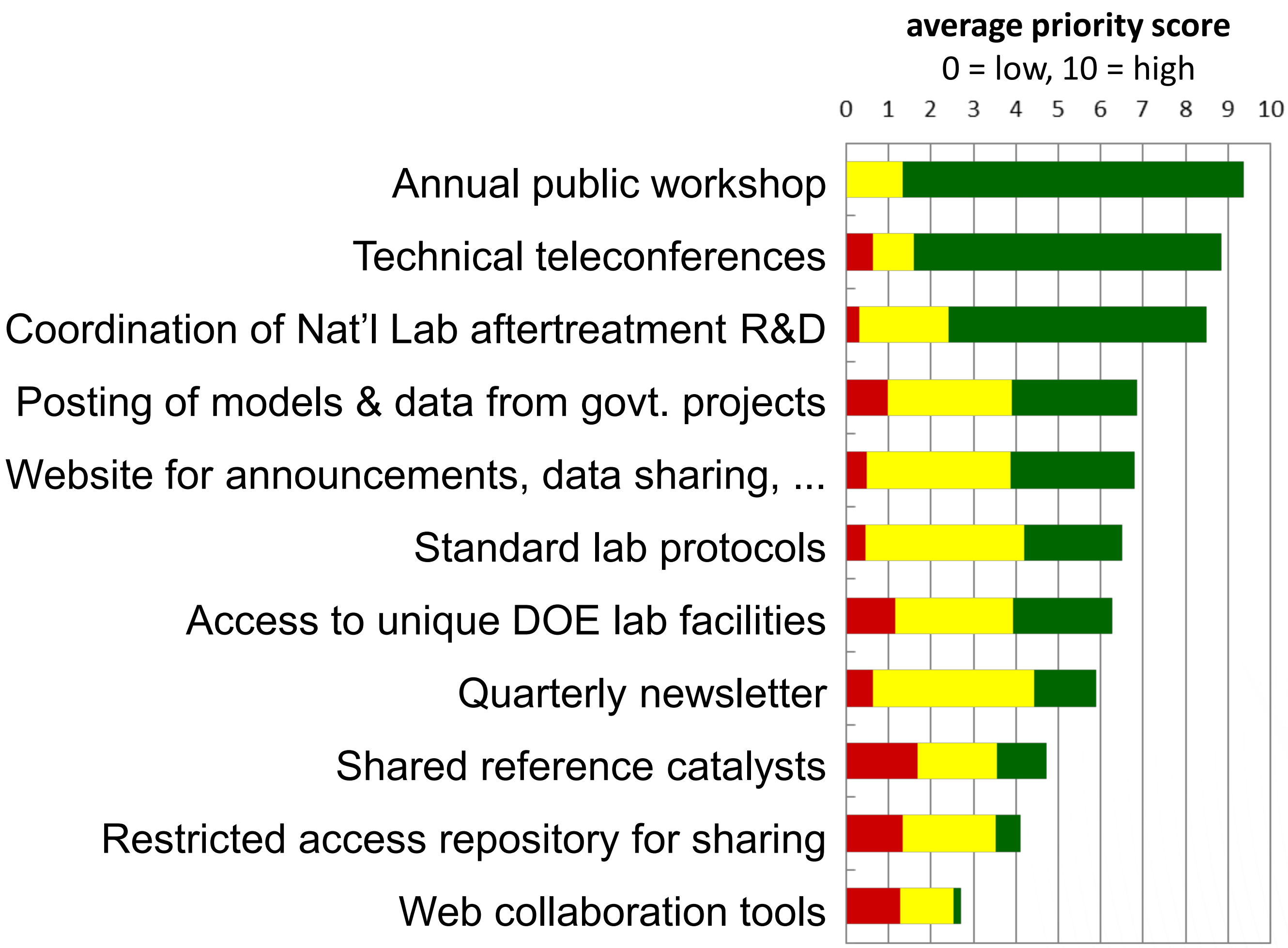
Summary

- **Relevance**
  - CLEERS supports the development of accurate and robust simulation tools for the design, optimization, and control of next generation emissions control technologies, which reduce fuel use by enabling higher efficiency engine operation & advanced combustion concepts
- **Approach**
  - Organized technical exchanges based on Workshops, Focus Group teleconferences, industry surveys, Crosscut team updates, pre-competitive data & models
  - Multi-scale experiments and modeling of commercial catalysts under relevant conditions
- **Technical Accomplishments**
  - Well-attended Workshop and teleconferences; Crosscut Team reports; shared data and protocols; source for data and models for parallel DOE projects and industry partners
  - SCR catalyst NH_3 storage model based on adsorption isotherms that accurately captures effects of gas composition, temperature, and aging for two commercial SCR formulations
- **Collaborations**
  - PNNL; Politecnico di Milano; ICT Prague
  - Collaborations among industry, universities, national labs through CLEERS organization
- **Future Work**
  - Continue coordination activities: workshop, telecons, website, priorities survey
  - Initiate characterization of passive adsorber materials and protocol development

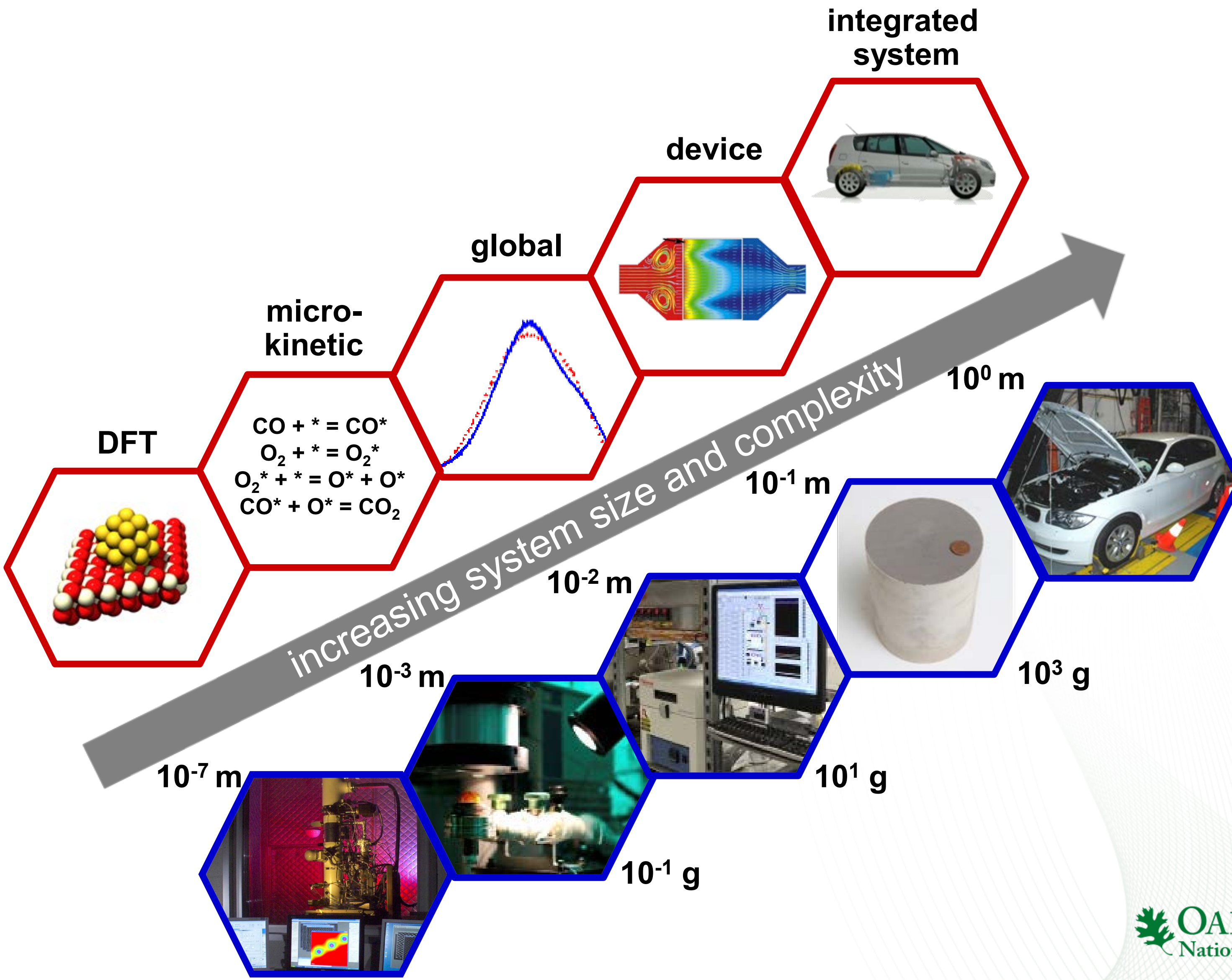
pihlja@ornl.gov

Technical Back-Up Slides

2015 Priority Survey confirmed a high level of interest in the core CLEERS organizational activities



DOE National Labs provide unique capabilities in multi-scale integration, ability to share precompetitive information across entire emission control community



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Questions? Comments?

pihlja@ornl.gov